

*The Photo-electric Behaviour of Iron in the Active and Passive State.*

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The discoveries of Hertz and of Hallwachs showed that a polished metal plate exposed to ultra-violet light readily loses a negative electric charge, but retains a positive charge. If an electric field is applied by making the metal form one plate of an air condenser, whose second plate is charged positively by a battery, the saturation current obtained may be regarded as a measure of the photo-electric activity of the metal.

It has been known for more than a century that ordinary iron, which is acted on energetically by dilute nitric acid, can be made to assume a passive condition by immersion in strong nitric acid. The same condition can be produced by other powerful oxidising agents, or by using iron as the positive electrode in an electrolyte containing oxygen. The nature of the change that takes place when iron passes from the active to the passive state has given rise to much discussion, but none of the explanations suggested has yet met with general acceptance.\*

The experiments to be described were carried out in order to compare the photo-electric activity of iron in the active state with that of the same sample in the passive state. It was hoped that the results might throw some fresh light on the theory of "passivity." The experiments prove that iron which is chemically active is active in the photo-electric sense, while iron which is passive shows much smaller photo-electric activity, in some cases none that can be detected. The bearing of these results on the nature of "passivity" will be discussed later.

*Measurements of the Photo-electric Activity.†*

The photo-electric activity of the plate under test was measured by determining the rate of leak between the plate and a parallel gauze of iron wire charged to 100 volts. The current was found by observing the

\* Useful summaries of the literature of "passivity" have been published by Heathcote ('Soc. Chem. Ind. Journ.', 1907, vol. 26, pp. 899—917) and Byers ('Amer. Chem. Soc. Journ.', 1908, vol. 30, pp. 1718—1742).

† I am indebted to the Government Grant Committee of the Royal Society for some of the apparatus used in this research.

rate of movement of the needle of a Dolezalek electrometer with one set of quadrants in connection with the plate. A mercury vapour lamp of fused quartz by Heraeus was used to illuminate the plate through the meshes of the gauze. Before commencing a series of observations the lamp was allowed to burn at least 20 minutes so that it might assume a steady state. In this paper the photo-electric activity of the iron plate is expressed in terms of the activity (arbitrarily assumed as 100 units) of a standard plate of pure silver supplied by Messrs. Johnson, Matthey and Co. Previous experiments by the author\* proved that this silver plate showed no photo-electric fatigue when kept in an air-tight brass testing vessel.†

The iron plates used in these experiments were cut from Kahlbaum's sheet iron, 0·2 mm. thick. They were in the form of circular discs 5·1 cm. in diameter, a projecting piece 2 cm. long and 1 cm. wide being left at one part of the rim to serve as a handle. In some cases smaller plates (3 cm. in diameter) of the same shape were used. Rods of commercial iron and steel were also examined. The rods, which were 5 cm. long and 0·6 cm. in diameter were polished in the lathe with fine emery paper. As all the tests for photo-electric activity had to be made with a dry plate, it was necessary, after having rendered the iron passive, to dry it without destroying the passivity. The method followed was that recommended by Heathcote. The passive iron was washed by the following solutions in turn :—

1. Saturated aqueous solution of potassium bichromate + 2·8 grm. potassium hydrate per 100 c.c. solution of bichromate.
2. Water 100 c.c., pure methylated spirits 10 c.c., potassium hydrate (by alcohol) 2·5 grm.
3. Absolute alcohol.

The solutions were sprayed or poured on to the plate as quickly as possible one after the other. The manipulation was easier for the rods than for the plates, and easier for the small plates than for the large ones.

In Heathcote's experiments the following test was employed in order to determine whether the iron plate was in the active or in the passive state :—

"The rod was regarded as passive when, after plunging in 1·2 nitric acid and shaking for a moment in the acid and then holding motionless, no chemical action could be detected at the surface by the unaided eye, the temperature of the acid being about 15°—17° C."

In the present experiments little difficulty was found in applying this test in the case of wires, small plates or rods. A passive wire or small plate could be kept in this dilute acid for some time without chemical action, but

\* 'Phil. Mag.', 1910, vol. 20, p. 570.

† 'Roy. Soc. Proc.', 1907, A, vol. 78, p. 484.

with the larger plates chemical action generally set in after the iron had been immersed for 15 or 30 seconds. A single spot of active iron is sufficient to start the reaction, and the difficulty experienced with the larger plates is probably due to the extent of the sharp edge forming the circular boundary of the plate.

*Summary of Experimental Results.*

The experiments in which plates of Kahlbaum's iron were rendered passive by immersion in strong nitric acid (specific gravity, 1.5) proved that such treatment reduced the photo-electric activity to considerably less than one-half of the value for the active plate, and that when reduction was most marked the plate was most distinctly passive.

The following extracts from the laboratory note-book illustrate the results:—

PLATE F, diameter 5·1 cm. :—	Photo-electric activity.
Plate cleaned with nitric acid and water, washed under tap, and then with solutions 2 and 3.....	144
Plate begins to dissolve at once in dilute nitric. Transferred to strong nitric, where action soon stops. Wash with solutions 1, 2, and 3.....	11
Plate tested in dilute nitric, is passive for 30 secs. Wash under tap and then with solutions 2 and 3 .....	70
Another experiment. Initial activity of plate .....	98
Dry iron plate, immersed in strong nitric, then washed with solutions 1, 2, and 3 .....	13
Plate tested in dilute nitric, remains passive about 5 or 10 secs. Washed under tap, and while <i>wet</i> placed in strong acid. Wash with solutions 1, 2, and 3 .....	18
Plate remains passive for 10 secs. in dilute acid. Wash under tap and then with solutions 2 and 3 .....	147

Results of a similar character were obtained with the rods of commercial iron and steel. The photo-electric activity, measured after treatment with strong nitric acid, was extremely small, and in some cases too small to be detected.

Experiments were also carried out in order to compare the behaviour of iron after being used as anode, and after being used as cathode, in a voltameter containing dilute sulphuric acid. According to Heathcote (*loc. cit.*): "The current density must be above a certain value for passivity to ensue. Iron behaves as if one could teach it to become passive; repeated trials end in success, and, once passivity has been produced, its reproduction is facilitated." "If the anode be sprayed with alkaline potassium bichromate solution as it is withdrawn from the sulphuric acid, it can be dried and kept 15 hours in a laboratory atmosphere without becoming active to 1·2 nitric acid."

By using small plates of Kahlbaum's iron, I have been able to show that photo-electric activity after use as anode is extremely small, but the experiments with the larger plates were not successful. In consequence of the difficulties in manipulating these plates, the later experiments were carried out with cylindrical rods of iron and steel. The rod formed one electrode, and was surrounded by a cylinder of thin sheet iron, which constituted the second electrode. In this way all parts of the rod were acted upon similarly. The rod was mounted so that it could be lifted vertically out of the voltameter, and washed with the solutions, without any risk of its coming into contact with the second electrode. The current was supplied by four secondary cells, giving 8 volts, and an ammeter and adjustable resistance were included in the circuit.

IRON ROD :—	Photo-electric activity.
Initial activity .....	60
Iron rod made cathode for 1 min., current 0·5 ampère, then washed with solutions 2 and 3 .....	80
Iron rod made anode for 1 min., current 0·5 ampère, then washed with solutions 1, 2, and 3.....	Less than 4
Iron rod made cathode for 1 min., current 0·5 ampère, then washed with solutions 2 and 3 .....	70
Iron rod made anode for 1 min., current 1·0 ampère, then washed with solutions 1, 2, and 3.....	Less than 2
Rod immersed in dilute nitric, not visibly acted upon at the moment of immersion, but action quickly begins.	

A steel rod gave similar results.

#### *Discussion of Results.*

The results just recorded may be summarised by saying that processes which render iron active in the chemical sense give it large photo-electric activity, while processes which render iron passive tend to greatly diminish the photo-electric activity, in general to less than half the value observed with an active plate. It must be borne in mind that in these experiments the photo-electric activity is measured with a dry plate, while the chemical activity is tested in solution, and that the processes employed in changing the state of the iron are all wet processes. We may extend our conclusions by including the observations of Muthmann and Frauenberger,\* who state that "metals become passive on lying in the air, and their potentials (in KCl solution) assume medium values, whilst vigorous mechanical cleaning of the surface renders them active." Here the reference is to chemical activity, but the statement is equally true if interpreted of photo-electric activity.

\* 'Zeit. Elektrochem.,' 1904, vol. 10, pp. 929, 930.

Metals exposed to the air show photo-electric fatigue, whilst polishing the surface gives rise to a large photo-electric current.

We appear to be justified in assuming a correlation between these two sets of phenomena and in saying that the chemical activity and the photo-electric activity vary together. If this view be correct we see that there are degrees of activity and also of passivity, a conclusion which appears to be in accordance with the general experience of chemists. Further, we may regard the photo-electric fatigue sometimes observed with iron as a gradual passage from the active to the passive state. The experiments of the author\* and others support the conclusion of Hallwachs that the principal cause of fatigue is to be found in the condition of the layer of gas at the surface of the plate. We should, therefore, be inclined to attribute passivity to the surface film of gas. The fact that from the photo-electric standpoint different degrees of activity can be obtained from the same iron plate does not harmonise well with the idea of an allotropic change as the cause of chemical passivity; it agrees far better with the idea of a protective coating, whether of oxide or of gas, and best of all with the last named, *i.e.* a gaseous film.

It must, of course, be admitted that such an explanation, whether applied to passivity or to photo-electric fatigue, cannot be regarded as final or complete until we are able to describe with greater definiteness the character of the modification in the gaseous layer to which the effects are attributed.

#### *Conclusion.*

1. The investigation into the photo-electric behaviour of dry iron shows that when the iron is chemically active it exhibits large photo-electric activity, while in the passive state this activity is greatly diminished.
2. It is held that this result is in good agreement with the theory which attributes passivity to the condition of the gaseous layer at the surface of the metal.

\* 'Brit. Assoc. Rep.,' 1910; 'Phil. Mag.,' 1910, vol. 20, p. 572.

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